COMPARATIVE TESTING OF HALON 1301 SUBSTITUTES USING A METHOD FOR ASSESSING TOXIC HAZARD

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Gaseous extinguishing agents **(GEA),** which have been used on the territory of the Russian Federation are subject to mandatory certification. The quality control of an extinguishing gas with a view to certify it is performed in accordance with the requirements of relating normative documents (Fire Safety Code "НПБ 51-96 " /1/ and others). However, the toxic hazard of a GEA in its actual use still remains outside of the range of controlled characteristics. Normative documents in force do not contain any requirements regarding the values describing toxic hazard or methods and criteria for toxic hazard evaluation.

To fill the gap, an approach for assessing toxic hazard of **GEAs** intended for use in total-flooding extinguishing systems has been developed at the All-Russian Fire Protection Institute (VNIIPO). Taking into consideration the conditions typical of total flooding, the approach is considered to be valid when the following assumptions are made:

- the concentration of a **GEA** in a protected enclosure **is** close to the normative extinguishing concentration
- a person does not remain for a long time in the extinguishing atmosphere
- a sharp increase in the hazard of the atmosphere during a fire extinguishment may occur due to generation of thermal decomposition products of a GEA

The essence of the approach consists in testing a **GEA** in the extinguishing concentration for obtaining data for use in assessing the toxic hazard of the GEA and its thermal decomposition products. A test installation has been developed for testing **GEAs** (Figure 1). The major parts of the installation are as follows:

- test chamber in the form of a parallelepiped with a volume of 1 m^3 and dimensions of 1.50 x 0.66 x 1.00 m. The chamber is made of sheet steel and its surfaces are enameled
- arrangement for supplying a GEA to the test chamber consisting of a standard reservoir with a volume of not less than 0.001 m^3 and **a** pipe with two offsets that have perforated nozzles at their ends and end in the interior of the chamber
- animal box equipped with a detachable cover made of a transparent material for observing animals during the testing and a door for isolating the box volume from the test chamber volume prior to the exposure of animals
- steel cylinder with a 0.045 m height and an open surface area of 0.01 m^2 containing 50 ml of *n*-heptane as a fire load. The combustible liquid is poured on the surface of a 20 mm high water layer. A remote spark igniter is used to ignite the *n*-heptane
- thermoelectric thermometer with a recorder capable of measuring temperatures in a range of between **–SO** and +100 °C

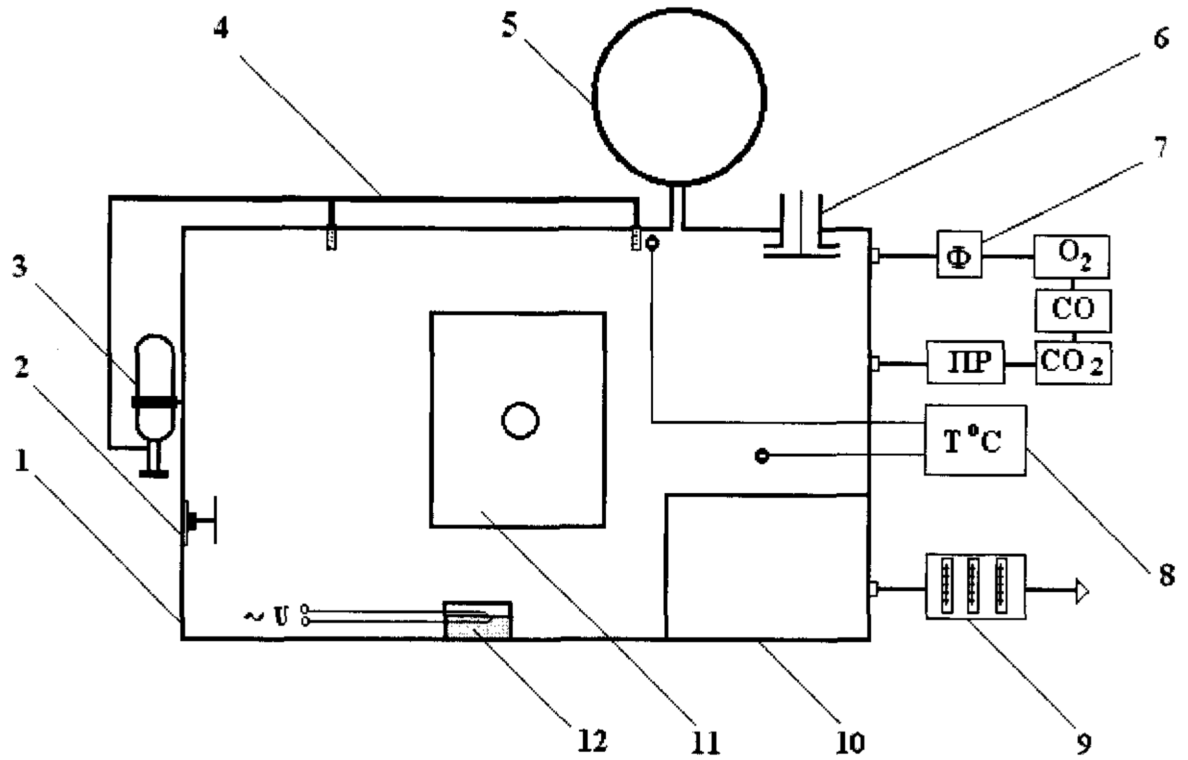

Figure 1. Schematic drawing of the test installation: 1 - test chamber; 2 - fan for mixing gases; **3** - reservoir containing an extinguishing agent; 4 - pipe: 5 - rubber bag for compensating the overpressure of gases; ***6***- blowthrough valve; 7 - line for connecting automatic gas analyzers (@- filter for gas purification, ΠP- pump) ; 8 - thermoelectric thermometer; 9 - sampling arrangement for decomposition products analysis; 10 - animal box; 11 - door with a window; 12 - combustible liquid; U - connection of a spark igniter.

Two types of test conditions are used for testing a **GEA** with the developed installation. Testing under the "cold experiment" conditions is reduced to the 1.5-min exposure of the animals to the atmosphere containing a **GEA** in the normative concentration for extinguishing n-heptane flame. Under the other test conditions that simulate a fire extinguishment, the 1.5-min exposure of the animals to the atmosphere generated in the test chamber after applying the **GEA** for extinguishing the n-heptane flame is used. In these test conditions the time of free combustion of the n-heptane is limited to 30–60 s and the **GEA** discharge time is limited to 10–15 s.

A list of data to be obtained from a **GEA** testing includes information that could be used in an analysis of the capacity of a person in an extremely dangerous situation to escape from a hazardous zone **(GEA** distribution zone) without any critical consequences to personal health. This list shall contain in particular the following data:

- survivability of the animals, changes in the animal behavior and condition observed during the exposure and 14-day post-exposure period
- capacity for physical work measured as the periods of time the white mice can swim a distance of 1.5 m in a water-filled pool until fatigue
- heart rate and rhythm for the white rats obtained by electrocardiography

- breathing rate and rhythm for the white rats recorded by a thermoelectric sensor located at the nasal part of animal's head
- hydrogen fluoride concentration obtained by ionometry using a selective electrode for fluoride ions

Hydrogen fluoride is included in the list of data due to its great toxicological significance since it is one of the most hazardous components of the decomposition products of fluorinated combustion inhibitors (halons. a number of their substitutes, sulfur hexafluoride).

According to the suggested assessment criteria, three degrees of the toxic effect hazard generated in actual use of a **GEA** are identified. Table 1 gives the basic characteristic for each hazard degree and expected results of a GEA testing corresponding to each hazard degree. Assigning a hazard degree to a **GEA** is made by comparing the extinguishing concentralions with those causing such disturbances in ***a*** person s condition that are critical with regard to survival. The probability of a generation of toxic concentrations of a GEA thermal decomposition products is also to be taken into consideration.

Comparative testing of Halon 1301 and HFC-125 and HFC-227 was conducted in accordance with the approach suggested. Clean agents (containing not more than 0.5 % of contaminants) were delivered as liquefied gases in standard reservoirs. Design concentrations of Halon 1301, HFC-I 25, and HFC-227 (approximately 5, 9.7, and 7 vol% respectively) were achieved in the test chamber using a controlled weight flow of gases.

"Cold testing" of the agents did not record any deaths or clinical signs of intoxications of the test animals. A short exposure to the extinguishing concentrations of Halon 1301 did not cause any changes in the behavior of the animals, their capacity for physical work and other signs giving an indication of the status of the animals. The effect produced by the alternative extinguishing agents manifested itself in the signs of mild irritation of the animals' respiratory organs. Besides, the exposure to HFC-I25 caused an earlier fatigue of the white mice that was observed between the 10th and 20th swimming of a distance of 1.5 m.

Testing under the conditions simulating a fire extinguishment generated data on the content of HF in the atmosphere present in the enclosure after applying a GEA for extinguishing the *n*-heptane flame (Table 2).

Comparative analysis of the test results shows a significant difference in the concentrations of HF generated in tests using different halogenated hydrocarbons for extinguishing *n*-heptane flames. Comparison of the concentrations of HF determined in testing HFC-I25 and HFC-227 to those determined in testing Halon I301 indicates that the concentration values may differ up to 7-11 times. Such a great difference in the obtained values of the HF concentrations confirms the existing information regarding a higher level of a potential hazard of non-brominated hydrocarbons, since toxic products may be generated as a result of their thermal decomposition /2,3/. The test results in Table 2 indicate that HFC-I 25 is more than HFC-227 prone to yield HF when contacting the *n*-heptane flame. The yield of HF in the experiments using HFC- I25 was 1.5 times higher than that in the experiments with HFC-227 when equal masses of the two halogenated hydrocarbons were used to extinguish the n-heptane flames.

TABLE 1. CRITERIA FOR ASSESSING TOXIC HAZARD FROM A GEA IN TOTAL-FLOODING CONDITIONS.

Degree of GEA hazard	Basic characteristic	Biological effects and concentrations of the decomposition products during testing
1	The value of the extinguishing volume concentration of a **GEA** is higher than the value of the dangerous concentration for human life at a short exposure.	For a short (15-minute) exposure of the test animals to a **GEA** in the extinguishing volume concentrations apparent disturbances in the status of the animals may be observed and/or a significant decrease in their capacity for physical work is determined.
2	The value of the extinguishing volume concentration of a **GEA** is lower than the value of the dangerous concentration for human life but toxic concentrations of the **GEA** thermal decomposition products may be generated in a fire extinguishment.	Symptoms of a heavy intoxication (with probable deaths in a group of the test animals) may only occur in a **GEA** testing simulating a fire extinguishment. The concentration of HF is higher than 40 $mg \cdot m^{-3}$.
3	The extinguishing volume concentration of a **GEA** is not dangerous for human life. The **GEA** thermal decomposition products do not produce any toxic effects or toxic effects are least probable.	Neither apparent symptoms of intoxication nor changes in the status of the animals that might give an indication of a significant reduction of their functional abilities are observed in a **GEA** testing simulating a fire extinguishment. Thermal decomposition products are absent or the concentration of HF is not higher than 40 $mg \cdot m^{-3}$.

Table 3 contains the results of the tests simulating a fire extinguishment in which animals were used. The results show that no cases of animal deaths, visible signs of intoxication, and statistically significant changes in capacity for physical work of the white mice were recorded in the experiments with Halon 1301. The observed decrease in the heart rate (which may be considered a response of an animal to the penetration of irritant gases into its respiratory tract) may only be taken as a symptom of an adverse effect caused by Halon 1301 and its thermal decomposition products. However, this observed disturbance of cardiac activity was moderate, was not accompanied by arrhythmia, and proved readily reversible within the first few minutes after the end of the exposure. Observations during the 14-day post-exposure period did not show any differences in data recorded for the control (intact) animals and those used in experiments (including the data on dynamics of animals weights). At the same time, the data indicate a high toxicity of the thermal decomposition products of the alternative agents (Table 3). Signs of heavy intoxication accompanied with obvious cardiac and respiratory disturbances were evidently observed in testing HFC-I25 and HFC-227 under the conditions simulating a fire extinguishment. Deaths of the animals were recorded during the 15-min exposure and 2-day post-exposure period; no statistically significant differences in the lethalities in the white rat samples were found for the two agents. On the contrary, the difference in the white mice lethalities proved to be the maximum probable (I 00 and 0%). To confirm the absence of deaths from intoxication, an additional testing of HFC-227 with the **use** of 10 white mice was conducted and again no deaths were recorded.

TABLE 2. CONCENTRATIONS OF HF IN THE TEST CHAMBER AFTER USING HALON 1301 AND ITS SUBSTITUTES FOR EXTINGUISHING THE *n*-HEPTANE FLAME.

Extinguishing agent	Amount of agent used in testing (g)	Concentration of HF ($mg \cdot m^{-3}$)
Halon 1301	310	20
	315	26
	315	36
	310	32
HFC-125	520	326
	520	260
	525	370
	525	320
	550	337
HFC-227	530	1x2
	550	215
	540	200
	550	210
	550	235

An analysis of the test results performed in consideration of the suggested assessment criteria (Table 1) shows that Halon 1301 corresponds to the third hazard degree whereas HFC-125 and HFC-227 correspond to the second hazard degree. This difference in toxic hazard degree is explained by a significant difference in the amount of thermal decomposition products of Halon 1301 and its substitutes and biological effects caused by these products. In spite of the fact that the same hazard degree was assigned to these Halon 1301 substitutes, some data show that HFC-227 is preferable to HFC-125 (from the safety point of view).

Table 4 contains reference data on the concentrations of HF corresponding to different hazard levels of this substance in emergencies. Comparison of this data with the test results presented indicates that the concentrations of HF measured in testing Halon 1301 under "fire extinguishing conditions" are close to the concentrations that still allow an evacuation of humans from a hazardous zone to be conducted without any irreversible injury to their health. Testing of the Halon 1301 substitutes under the same test conditions shows that the substitutes decompose yielding HF in the amounts generating an incompatible with life or problematic regarding survival atmosphere in the test enclosure. The experiments conducted occurred in a range of HF concentrations between 200 $mg \cdot m^{-3}$ and 370 $mg \cdot m^{-3}$, whereas Table 4 gives 2050 $mg \cdot m^{-3}$ as the value for the ALC. This significant discrepancy between the test results and reference data is probably due to generation of'other thermal decomposition products of HFC-125 and HFC-227 in addition to HF that may produce strong toxic effects.

TABLE 3. TESTING OF HALOGENATED HYDROCARBONS WITH THE USE OF ANIMALS UNDER TEST CONDITIONS SIMULATING A FIRE EXTINGUISHMENT.

Data to be determined	Agent used for extinguishing the n-heptane flame and its concentration		
	Halon 1301 5 vol%	HFC-125 9.7 vol%	HFC-227 7 vol%
Changes in general condition and behavior of the animals	Not visually observed	Signs of heavy intoxication: depression, dyspnea, typical spasm of respiratory tract, cyanosis. Death of animals during the exposure or within 2-day post-exposure.	Signs of heavy intoxication are more obvious in rats (loss of motion, dyspnea, cyanosis). Death of rats within the first day after exposure.
Physical activity of white mice	No change	Determination not undertaken	Determination not undertaken
Heart rate and rhythm in rats	Moderate bradycardia (30% decrease in heart rate) without arrhythmia	Significant bradycardia (80% decrease in heart rate), signs of acute cardiac insufficiency	Significant bradycardia (60% decrease in heart rate), arrhythmia
Breathing rate and rhythm for rats	Determination was not undertaken	3-5 times decrease in breathing rate: arrhythmical respiration; irregular respiration depth	3-5 times decrease in breathing rate; breathing arrhythmical, irregular
Lethality: Rats	Not observed	42 %	50 %
Mice	Not observed	100 %	Not observed

TABLE 4. TOXIC AND ALLOWABLE CONCENTRATIONS OF HF FOR SHORT EXPOSURES.

Concentration	Values of concentration	Ref.
ALC - Approximate Lethal Concentration for the 15-min exposure	2500 **ppm** by volume in air (2050 mg•m^{-3})	4
Dangerous concentration for short exposures	50-250 ppm by volume in air (40–210 mg•m^{-3})	4
IDLH–concentration immediately dangerous to life or health hut permits a person not equipped with breathing apparatus to escape within 30 min without irreversible health effects	30 ppm by volume in air (25 mg•m^{-3})	**5**
Maximum allowable concentrations in emergency conditions: 10 min	20 ppm by volume in air (17 mg•m^{-3})	6
30 min	10 ppm by volume in air (8.5 mg•m^{-3})	6

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